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Foams: From Nature to Industry

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“Invited contribution to Dominique Langevin Festschrift”.

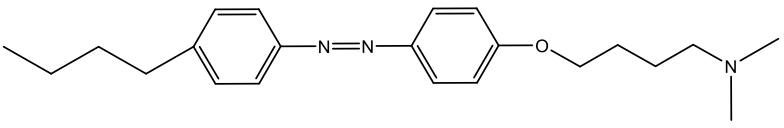
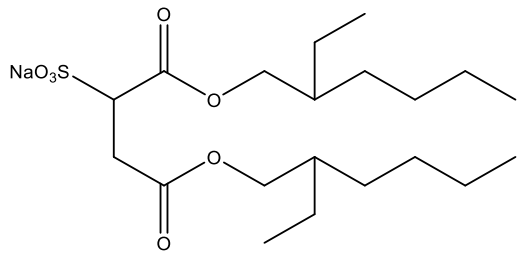
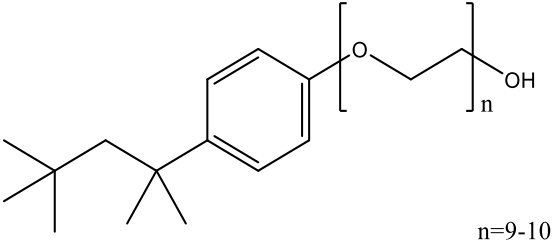
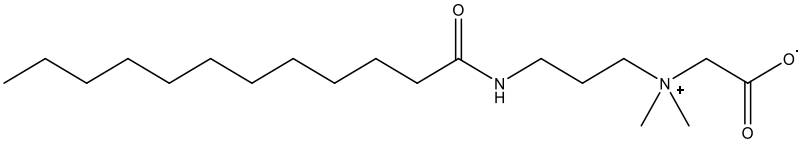
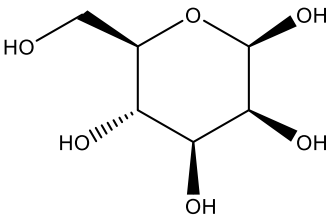
Abstract

This article discusses different natural and man-made foams, with particular emphasis on the different modes of formation and stability. Natural foams, such as those produced on the sea or by numerous creatures for nests, are generally stabilised by dissolved organic carbon (DOC) molecules or biological proteins. In addition to this, foam nests are stabilised by multifunctional mixtures of surfactants and proteins called ranspumins, which act together to give the required physical and biochemical stability. With regards to industrial foams, the article focuses on how various features of foams are exploited for different industrial applications. Stability of foams will be discussed, with the main focus on how the chemical nature and structure of surfactants, proteins and particles act together to produce long-lived stable foams. Additionally, foam destabilisation is considered, from the perspective of elucidation of the mechanisms of instability determined spectroscopically or by scattering methods.

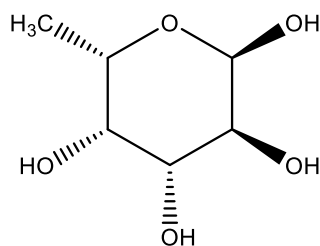
Keywords:

Foam stability, Foam destabilisation, Natural Foams, Man-made foams, Defoaming

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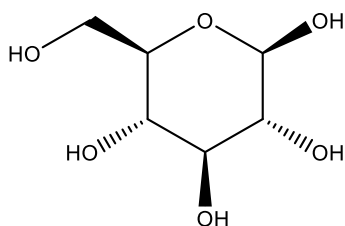
Name	Structure	Reference
4-butyl-4'-(4- <i>N,N</i> -dimethylbutoxyamine) azobenzene bircarbonate (AZO-B4)		[26]
Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT)		[65]
4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton X100)		[79]
[3-(Dodecanoylamino)propyl](dimethyl)ammonioacetate (Cocobetaine)		[79]
β-mannose		[85]

β-fucose



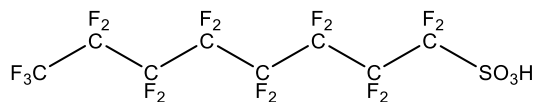
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β-glucose



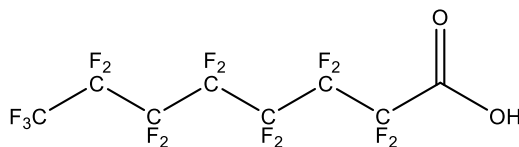
[85]

**Perfluorootanesulfonic acid
(PFOS)**



[106]

**Perfluorooctanoic acid
(PFOA)**



[106]

Table 1: Showing structures of chemicals referred to in this review.

1. Introduction

This article provides an overview of recent advances in aqueous foam science, with the major emphasis of the first half being on understanding both the stabilisation and destabilisation of aqueous foams. This important area is always expanding, and as a result on average over four thousand scientific articles have been published over the past five years in the area of foams. The sections of this review do not delve into the detailed physics associated with these processes, and it should be noted that many reviews exist providing in depth accounts of the fundamental science in this area: for example, and not limited to [1–6].

As a way to distinguish this article from other reviews, the second half focuses solely on the science of both natural and man-made foams. In the natural foam section, highlights will be made on how nature forms foams, often under harsh conditions and with high stability. For example, foam nests produced by different species of fish, frogs and insects have been found to be stable for up to ten days under tropical conditions.[7,8] These nests are essential for providing their young with the necessary protection and moisture during incubation.[9–13] In an industrial context, foams are often considered to be a nuisance and much work has been done in the area of defoaming to combat undesired foams.[14–18] However, although this article does discuss defoaming, the main focus is on the positive and practical uses of foams in industries such as fire-fighting, mineral flotation and other recent advances.

94 From an historic perspective, the earliest recorded works associated with foam science
95 were carried out during the nineteenth century by Belgian physicist Joseph Plateau.
96 Although Plateau has been recognised as the pioneer in the field, and did lay down
97 enduring foundations, surprisingly his publication [19] “Experimental properties of
98 liquids resulting from their molecular forces” makes only fleeting references to foams.
99 Plateau did establish the essentials, describing in his work how foams form within three-
100 dimensional frameworks, in addition to describing practical aspects of establishing foams
101 and outlining some of the underlying mathematics. The fundamentals, known as
102 Plateau’s laws, are:

- 103 1) The thin films are smooth, with a constant mean curvature
- 104 2) At a liquid edge (Plateau Border), no more than three films can come together and
105 they form an angle of 120°
- 106 3) The Plateau borders that come together in one point are always in the number of
107 four and foam angles of 109.5°

108
109 Since the nineteenth century, much work has been published on the subject of foams,
110 including many books publications which are recommended to the reader.[14,20,21]
111
112 A foam is generally defined as a dispersion in which a large proportion of gas by volume
113 in the form of bubbles is dispersed in a liquid, solid or gel, hence forming closed cell
114 structures. Foams have useful properties owing to their low density, very large surface
115 area and because they exhibit both solid and liquid like behaviour. They are ubiquitous
116 systems which have proved to be an essential part of our daily lives, playing key roles in
117 aqueous applications such a fire-fighting, mineral flotation, detergents as well as
118

applications such as upholstery, insulation, metal foams etc.[20] In addition, they can
 also be found in numerous instances in the natural world. Perhaps the most familiar
 natural examples are sea foams. When many aqueous systems are sufficiently agitated
 and begin to incorporate air foams may form, which are very weak and short lived.
 However, when stabilising agents, for example dissolved organic carbon (DOC) from
 decomposed organisms (e.g. plankton), are present long lasting foams are produced that
 can be seen being blown along the coast. So, in general, the presence of a foam is a good
 indicator of the occurrence of industrial or natural surfactants.[21]

Foams are referred to as being metastable, confusingly foams are also sometimes referred
 to being at equilibrium, however this is only used as a useful approximation due to the
 apparent rate of coarsening and destabilisation.[20] The structure of a metastable foam is
 determined by the minimisation of interfacial area for a given liquid volume fraction, and
 is determined by simple geometric rules at the scale of a film and a few bubbles. [2]

Figure 1 shows a photograph of a typical metastable aqueous foam, showing the effect of
 gravity on drainage and coarsening with height. The reason for this can be explained by
 considering the liquid volume fraction (ϕ , Equation 1), the key parameter used to describe
 the amount of liquid contained within a foam and therefore the shape of the bubbles. The
 other parameters equation 1 are the volume ratio of the liquid content (V_{liquid}) and the
 foam volume (V_{foam}). Physical and mechanical properties influenced by ϕ include,
 thermodynamic, acoustic, and rheological properties. Foams with ϕ higher than about 0.1
 are referred to as wet foams. Wet foams are found towards the bottom of the foam
 column around the air/ water interface and the bubbles are well approximated by
 contacting deformed spheres. Further away from the air/ water interface, for decreasing

values of ϕ , the bubbles become increasingly more distorted in shape. Foams with a volume fraction of less than 0.05 are generally referred to as dry foams and can be described by Plateau's laws. These dry foams consist of thin films that are normally idealised as single surfaces and are polyhedral in shape.[20] The reader is referred to a recent review on the structure and energy of aqueous foams for more information. [2]

Equation 1:
$$\phi = V_{liquid}/V_{foam}$$

The shape of an air/ water interface is determined by the existence of surface tension. In general the shape is determined from the Young Laplace law, Equation 2, where Δp is the pressure difference across the fluid interfaces, γ is the surface tension and R_1 and R_2 are the principal radii of curvature. The Young Laplace law states that the pressure difference between the two sides of an interface is equal to the mean curvature of the interface multiplied by surface tension. Surface tension acts to flatten the surface whilst the pressure difference tends to curve it.[21]

Equation 2:
$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

2. Foam Stability

Single component pure liquids are not generally suitable for producing foams due to the rupturing of fluid films almost immediately as a result of thermal or mechanical perturbations. As well as this, foams do not form spontaneously and energy is required to disperse the gas in the liquid to create bubble surfaces. The energy cost (W) is broadly the product of the surface tension (γ , J m⁻² or N m⁻¹) and of the area created (A , m²) as

shown in Equation 3. Foams are thermodynamically unstable systems that tend to separate with time under the influence of van der Waals forces and gravity.[22] The lifetime can be used to distinguish transient and metastable foams. Transient foams may last for a few seconds, but metastable foam lives can vary from minutes to years.[15] The key to producing metastable foams is to modify the surface properties by use of stabilising agents, such as surfactants, polymers, proteins or particles. The role of stabilising agents is to stabilise the foams with respect to the different destabilisation mechanisms, which will be discussed in more detail in section 3.

Equation 3:
$$W = \gamma \Delta A$$

In the next section, a brief overview will be provided on the main components used to produce stable foams. As well as this, comparisons on the stability of foams will be made between the four stabilising agents and mixed stabilised systems will be discussed. These next sections present the necessary information to set the scene for the rest of the article and are not intended to offer in depth accounts. For a more detailed review of foam stabilisation, the reader is referred elsewhere.[23]

2.1 Surfactant-Stabilised Foams

Most foams owe their existence to the presence of surface active agents or surfactants that accumulate at interfaces. Surfactants are used to reduce the surface tension and importantly when considering foams, stabilise the thin films against rupture.[20] The phenomenon of surface tension arises due to an imbalance of attractive intermolecular interactions at the surface of a liquid, and consequently creating an interface between a liquid and a gas requires additional energy which is attributed to the surface tension

(γ). [21] Without this reduction in surface tension, the liquid could not be transformed from its bulk state, with a minimal surface area, into a high surface area foam. Since surfactant molecules are amphiphilic, when used to produce foams, the molecules adsorb at the air/ water interface until it is covered completely, with head groups in the water and tail groups in the air as seen in Figure 2. In the case of ionic surfactants, this results in the formation of two double layer distributions of charges consisting of a plane of negative heads and an adjacent diffuse cloud of positive counterions. The two adjacent air/ water surfaces in a foam are therefore covered by charged monolayers that repel each other, stabilising the foam at the thickness at which electrostatic attractions and van der Waals interactions are balanced. [21] The opposing electrostatic and van der Waals forces are typically balanced for film thicknesses in the range of 10–1000 nm. The wavelengths of visible light lie squarely in this range, resulting in the familiar result shimmering interference colours. [24]

To achieve high foam stability and quality using surfactants, it is believed that the surfactants must be above their respective critical micelle concentrations (CMCs). [25] For many industrial processes, using these high concentrations can be costly. Recently Derikvand *et al.* [25] investigated how increasing the concentration of a low-cost polymer (carboxymethyl cellulose gum) to a fixed concentration of commercial anionic surfactant solution (0.25 wt%) would improve the foaming ability and stability. In altering the polymer concentration from 0.000 – 0.625 wt%, foam lifetimes were found to improve significantly. The reason for this increase in foam lifetime and stability was understood to be due to the repulsion between the anionic polymer and anionic surfactant. As well,

the addition of polymer increased the film elasticity and decreased permeability of gas within the foam therefore reducing effective coalescence of the bubbles.

Dual stimuli-responsive surfactants have also been developed recently to achieve so called smart foams which can be stabilised and destabilised by CO₂/N₂ and light as shown in Figure 3. [26] The novel surfactant developed by Jiang *et al.* name AZO-B4 (Table 1) contains tertiary amine and azobenzene which are moieties affected by the external stimuli. CO₂ in water converts the hydrophobic tertiary amine to surface active amphiphilic ammonium bicarbonate group, whereas the N₂ makes the surface active form return to the un-ionized form with lower surface activity. UV radiation was found to convert the trans-form of the molecule to the cis isomer, which also influenced the hydrophobic-hydrophilic balance. A significant difference was observed in the properties when comparing AZO-B4 before and after UV illumination. Before UV illumination, AZO-B4 had a surface tension of 32 mN m⁻¹ and a CMC of 2.3 x 10⁻⁴ M, whereas after illumination the surface tension had increased to ~35 mN m⁻¹ and the CMC had increased by ~20 times. This significant difference explains the large decrease in foam stability after illumination since the AZO-B4 is less surface active after being subjected to UV. No foaming was observed when AZO-B4 was purged with N₂, however when bubbling CO₂ through the solution foam could be regained as the tertiary amines were converted to surface active ammonium bicarbonate salts. This type of reversible multi-stimuli responsive system will be of much interest for industrial applications where control of the stabilisation and destabilisation of foams is imperative.

2.2 Protein Stabilised Foams

Protein foams play an integral role in many processes in the beverage and food industries, fire-fighting as well as natural processes such as the formation of foam nest for the protection of frog eggs during fertilisation processes. With all these applications, protein foams must first obtain the desired level of foamability, and then maintain stability when subjected to a variety of dynamic processes. Therefore, factors determining foamability and stability to mechanical and thermal processing are important to applications of protein foams.

Population of an air/ water interface by protein molecules involves adsorption followed by conformational changes, referred to as surface denaturation. These processes are the subjects of considerable investigation in order to gain insight into the mechanism of foam stabilisation. For a protein to be a good foaming agent it must, most importantly, be soluble.[27] Additionally, the protein may have to unfold at the interface, exposing hydrophilic and hydrophobic residues to straddle the interface. There is evidence indicating that the ease of protein unfolding and the accessibility of hydrophobic residues are closely related.[28,29] Additionally, surface hydrophobicity has been correlated with improved foaming properties.[28,30,31] When a protein adsorbs at an interface, hydrophobic interactions are directed towards the non-aqueous side of the interface, and the protein loses tertiary structure but retains much of its secondary structure.[32] The phenomenon of adsorption is thermodynamically favourable due to the simultaneous dehydration of the hydrophobic interface and hydrophobic portions of protein.[32] Once contacts are made with the interface, natural flexibility within the molecules can expose

previously buried hydrophobic portions, leading to the desired interfacial denaturation of the protein.[33] Recently the effect of limited hydrolysis and glycation (the non-enzymatic reaction between reducing sugar) of bovine β -lactoglobulin on the stability of foam has been studied as a way to further improve the applicability of the protein.[34] Corzo-Martínez *et al.* were able to show that the protein effect on foaming capacity was insignificant when subject to both limited hydrolysis and glycation at both pH 5 and 7. The stability due to of the foams at pH 5, however, was greatly improved showing enhancements in the levels of drainage when compared to non-hydrolysed bovine β -lactoglobulin. The improvement in foam stability was attributed to an increase in the elastic character of the protein, which was indicated by an increase of the surface dilation modulus.

The proteins used are less ionisable and less abundant than typical ionic surfactants. For this reason, electrostatic repulsions are generally not strong enough to support stable protein foams. Instead, a dynamic mechanism known as the Gibbs–Marangoni effect confers a stabilization effect. This effect is optimised when absorbed proteins are efficient at changing the surface tension. As illustrated in Figure 4, a suddenly stretched film has a lower protein concentration and hence a higher local surface tension. The gradient in surface tension induces a flow of liquid that has been found to delay destabilisation mechanisms such as drainage and coalescence.[24] In some protein stabilised foams, there can be extensive intermolecular interactions between the protein molecules. These forces lend to cohesive films at the interface which act to reduce or stop foam drainage.[35]

Proteins differ from low molecular weight surfactants in that:

- They adsorb at an interface at very low concentrations, and there is a possibility of more than one layer of protein molecules being adsorbed
- Flexible protein molecules can change their conformation when they adsorb
- Protein molecules can be relatively easily desorbed from an interface when they are displaced by means of low molecular weight surfactants

Due to these differences, there are several consequences when proteins are adsorbed at a liquid interface compared to surfactants. Hydrophobic portions of the protein can form trains at the interface, whereas hydrophilic parts form loops and tails in the liquid sub phase. The involvement of many protein segments in the adsorption process means that it takes a relatively long time before the equilibrium conformation of the adsorbed molecules is reached. This has important consequences for the surface behaviour under dynamic conditions.[36]

2.3 Particle Stabilised Foams

It has been known from many years that colloidal particles possess surface active properties and can adsorb spontaneously at air/ water and liquid/ liquid interfaces. [5] Ramsden[37] and Pickering[38] were the first to realise this at the beginning of last century. Although most colloidal particles are surface active, they are not amphiphilic like surfactant molecules. The exceptions, however, are the so-called Janus particles: the surfaces of these particles present two regions with differing wettabilities, so regions that are hydrophilic and hydrophobic zones.[39]

In the context of foams, particles can be used to produce stabilised aqueous foams under dynamic conditions. In contrast to surfactants, adsorption of particles at an air/ water interface does not change the surface tension of the system; instead it reduces the total surface energy hence contributing to the stability.[40] There are some advantages of using solid particles as opposed to conventional surfactants in the formation of foams. One advantage is due to the improved bubble stability towards destabilisation mechanisms such as coalescence, coarsening and drainage therefore forming more robust thick foams.[41] Parameters of importance for particle stabilised include: the nature of the particles, their size, shape, concentration, hydrophobicity, surface charge, state of aggregation, surface area and density. However, the key parameter in the case of adsorption of spherical particles to interfaces is thought to be the contact angle (θ). Given a sufficient angle θ , the adsorption energy per particle can be high enough (~ 2000 KT) so that once the particles are adsorbed at the interface of a foam, it is almost impossible to force them out.[42] This is a vast contrast to surfactants that adsorb and desorb on a relatively fast timescale. Equation 4 helps to explain this by the energy of attachment of a solid particle at the air/ water interface:

Equation 4:
$$E = \pi R^2 \gamma (1 \pm \cos \theta)^2$$

Where R is particle radius, γ is surface tension and θ is contact angle of particle to the liquid. The equation tends to put the desired contact angle in the region of 90° , so that the particles are not particularly preferentially wetted by either the dispersed or the continuous phase.[43] Additionally, the contact angle has been found to increase with the particle hydrophobicity.[44] For hydrophilic particles, θ measured into the aqueous

phase is normally $< 90^\circ$ and a larger fraction of the particle surface resides in water than in the air phase. For hydrophobic particles, θ is generally greater than 90° and the particle resides more in air than in water. By comparison with surfactant molecules, the monolayers will curve such that the larger area of the particle surface remains on the external side, giving rise to air or oil in water when $\theta < 90^\circ$ and water in air or oil when $\theta > 90^\circ$. [5] Interfacial forces arrange particles into various structures in liquid films thus inhibiting coalescence. Typically, there are six different particle arrangements that can effectively separate the air/ water interfaces as seen in Figure 5.[45]

- Closely packed single layer of particles (CP1), Figure 5 (a)
- Loosely packed single layer of particles (LP1), Figure 5 (b)
- Closely packed double layer of particles (CP2), Figure 5 (c)
- Loosely packed double layer of clustered particles (LP2C), Figure 5 (d)
- Closely packed 'double+' layer of particles (CP2+), Figure 5 (e)
- Loosely packed 'double+' layer of clustered particles (LP2+C), Figure 5 (f)

Solid particles were initially used in combination with surfactant molecules to generate adsorption at solid/ liquid interfaces and they were used for both stabilisation and destabilisation of foams.[5,46–48] It is only been in the last 10 years or so that foams solely stabilised by nanoparticles have been reported, with Binks and Horozov pioneering the field.[44] In this work, Binks *et al.* obtained very stable aqueous foams by using near spherical fumed silica nanoparticles with diameters ranging between 20-50 nm which were hydrophobised by silanization of hydrophilic silica with dichlorodimethylsilane to different extents to investigate the effects of particle hydrophobicity on foam stability in

the absence of any surfactant. The foams were prepared by several different methods which all yielded stable foams when particles with intermediate hydrophobicity were used. The foam stability is enhanced due to the particles present in the aqueous phase collecting in the Plateau borders, slowing down film drainage. Thus, showing a maximum in the foaming ability with respect to the hydrophobicity of particles. Optical microscope images revealed that the foam contained micron-sized non-spherical bubbles (5-50 μm) surrounded by branched particle aggregates. Similar results were obtained by Alargove *et al.* who produced foams that were stabilised by polymer microrod particles.[49] Their results showed no loss of gas and only a slow decrease in liquid volume during the first 24 hours as a result of water drainage and bubble compaction. Therefore, the ability of the particles to stabilise foams in the absence of any other surfactant has been the subject of considerable attention recently, some of these interesting articles are recommended for further reading.[3,5,44,49–52]

3. Mechanisms of destabilisation

As just discussed in the previous section, the stability of foams depends on various factors and different materials or mixtures of materials can produce stable foams. Three of the most important processes, which will be discussed in more detail, govern the decay processes of foams: drainage, coarsening, or bubble coalescence. Figure 1 shows the effect of foam drainage, whereas Figure 6 shows how both coalescence and coarsening occur in foams. Much of the literature based on destabilisation describes the detailed physics, with differential equations being used to model the different mechanisms. The basis of this discussion will be the fundamental science behind each mechanism, with the main emphasis being on different spectroscopic techniques that have been used. For

example, Delago-Sánchez *et al.*[53] have developed a technique that has been able to detect the three foam destabilisation processes. Their work was carried out by utilising a laser and applying it to the surfactant stabilised tannin-based liquid formulation foam. Due to the studied samples being opaque, only backscattered light was detected as a function of time and position along the tube and this could be used to determine foam stability. Their results, based solely on changes in the amount of backscattered light could show the region in which drainage is occurring compared to coarsening and coalescence. Additionally, optimised conditions for both stirring time and surfactant concentrations were identified.

3.1 Drainage

Drainage is defined as the irreversible flow of liquid through a foam through film membranes via Plateau borders under the influence of both gravity and capillary forces. As water begins to drain under gravity, the top of the foam quickly becomes dry, with less than 1% liquid, whilst the bottom remains wet. The shape of the bubbles begins to change under the influence of drainage, going from a somewhat spherical shape which distorts the bubbles into polyhedral shapes. This drainage mechanism leads to foam gas bubbles becoming less stable, and increasingly susceptible to bursting.[54–60] When foam drainage is hindered, however, foam stability can be drastically improved.[59] This has been found to be achievable if the liquid bulk viscosity is relatively high, if the surface-active material is able to rigidify the film surfaces by formation of highly condensed and insoluble monolayers, or if a microgravity environment is used.

415 Dry foams are quite amenable to theoretical treatment, so that most of the formalism
416 developed may be regarded as an expansion about the dry foam limit. Verbist *et al.* for
417 example, have developed a description of foam drainage, in terms of a non-linear partial
418 differential equation for the foam density as a function of time and vertical position.[61]
419 Gravity poses difficulties for studying the drainage of wet foams, which has provided
420 recent motivation for experiments under microgravity.[59] Monnereau *et al.* studied two
421 systems during a parabolic flight campaign, one transient foam system containing a
422 surfactant-free organic liquid, and a stable foam system containing a mixture of both
423 sodium dodecylsulfate and dodecanol. At zero gravity, it was found that both foam
424 systems were stabilised, forming very wet foams with spherical bubbles which did not
425 change diameter during the flight. At 1.8 g, the transient foam collapsed, and although
426 the stable foam did not collapse, the bubbles became polyhedral and numerous
427 topological transformations were observed. A very recent review by Langevin [62] is
428 focused solely on foam and foam film studies that have been performed in gravity-free
429 conditions. For example, the stability of both surfactant and surfactant-free foams have
430 been studied on the International Space Station (ISS). These very interesting experiments
431 demonstrated how solutions that foamed only a little on Earth, had significantly increased
432 foam stability in space. High liquid volume fractions (30%) were observed as well as
433 decreased rates of drainage, coarsening and coalescence. The surfactant-free studies
434 showed how bubbly liquids made with pure water were able to remain stable over very
435 long periods of time, unlike on Earth. The reason for this increase in stability has been
436 attributed to the absence of drainage. Many more experiments have been discussed in this
437 review and it is highly recommended. [62]

Work has been conducted using X-ray scattering to study foam structure as well as destabilisation by drainage.[63,64] More recently, however, techniques such as neutron reflectivity and terahertz spectroscopy have been employed as more sensitive methods for studying foam drainage.[54,65] Heuser *et al.* were able to exploit the fact that water absorbs terahertz radiation, and were therefore able to successfully determine real time drainage rates based on water content at respective foam heights by using terahertz spectroscopy. Neutron reflectivity techniques are well suited for structural studies of aqueous foams, due to the large differences in scattering length density of protonated and deuterated materials, which can give very good structural contrast for the domains and layers. Ederth *et al.* used neutron reflectivity as a method to characterise the internal structure of foam films, by monitoring the drainage stages of an AOT film (Table 1). [59] Their results showed that a single bilayer is trapped within the film during late stages of drainage.

3.2 Coarsening

Coarsening refers to the process of growth and shrinkage of bubbles within a foam due to inter-bubble gas diffusion. During coarsening, the growth of the average bubble radius (R) with time (t) is represented by $R \sim t^{1/2}$. This is because the bubbles within a foam chose the smallest path to diffuse between thin films. [1] Although the driving force for coarsening is the Laplace pressure, there are many features that determine the rate of coarsening including liquid fraction, the average bubble size to the physical chemistry of the gas and the liquid.[21] The Laplace pressure for a spherical bubble is inversely proportional to its radius and is represented by Equation 5, where γ is the surface tension and R is the bubble radius. A recent publication by Dittmann *et al.* provides a good

summary of the differences between coarsening in both wet and dry foams, including the main equations that have derived to understand the theory behind coarsening.[66]

Equation 5:
$$\Delta P = 2\gamma / R$$

The characteristic coarsening time of a foam has been described in terms of many different properties such as: gas diffusivity and solubility constants, the bubble deformation, the liquid volume fraction content, thickness of the thin film, the initial diameter of the bubble and the solution surface tension.[1,67] Another major contributor to the characteristic coarsening time of a foam is the type of gas employed, which plays its part through the effective diffusion coefficient. Water soluble gases such as carbon dioxide give less stable foams than gases that are not so water soluble such as nitrogen. This is because carbon dioxide is able to transport across water films much more readily than nitrogen. Therefore, by adding small amounts of nitrogen to carbon dioxide produced foams, the stability can be increased due to the delayed gas diffusion process.[68]

Many different techniques have been employed to try and study the structure and dynamics of coarsening within a foam.[66,69–72] Earlier work undertaken by Durain *et al.* aimed to try and understand the structure and dynamics of three-dimensional foams by use of the direct and non-invasive technique multiple light scattering. Using this approach, Durian *et al.* were able to exploit the strong multiple light scattering of foams and directly probe the average bubble sizes. Their results identified some previously unrecognised rearrangements of the internal dynamics within the foam bubbles.

Furthermore, they developed a model for dynamic light scattering that was used to interpret temporal fluctuations in the intensity of multiply scattered light.[72]

As a way to circumvent the ‘model dependence’ of using multiple light scattering for studying the structure and dynamics of foams, magnetic resonance imaging (MRI) was used as a non-invasive probe of the foam interior. MRI was used by sampling the polarisation density of the nuclear moment as a function of position, enabling the reconstruction of the topology at continual stages of coarsening.[71] Results by Glazier *et al.* showed that 75% of the bubbles within the system of study had coarsened rapidly during an initial period of four hours after sample preparation. This changed to only 85% after another eight hours and declined very slowly after that. Again, there were problems associated with using this technique, namely due to the finite resolution achieved by MRI. This is because if some very small bubbles were not counted, their estimations of the average bubble size could have been inadequate.

More recently, Dittmann *et al.* were able to improve on previously conducted work[69,70] by using fast synchrotron phase-contrast micro computed tomography (μ CT) to study the aging dynamics of moderately wet protein foams.[66] The sections of previous work they were able to extend significantly were in the detail of analysis as well as the number of individually tracked pores and the time scale. Their work was successful in that they were able to capture 50,000 pores within the field of view and observe the individual dynamics of on average 39% of the pores within the different conducted time steps. As well as following the dynamics of the pores, they were able to show the radius dependent coarsening rates as two dimensional number histograms for

each time step, showing that a time independent rate was an adequate description of an individual pore growth dynamic.

3.3 Coalescence

The overall result of coalescence is the same as coarsening, as in there is an overall decrease in the number of bubbles. When drainage is complete, and the equilibrium liquid volume fraction has been reached, the thin films between bubbles are very thin (5-20 nm) and are more likely to rupture, leading to bubble coalescence. [1] However, instead of gas diffusing from one bubble to another until it completely disappears, coalescence occurs due to the rupturing of the thin films between bubbles, which leads to a decrease in gas volume within the foam until it completely disappears.[21] In comparison to drainage and coarsening, the process of foam coalescence is the least understood.

As a way to understand the role of both film size and liquid fraction in the coalescence of a foam, Carrier *et al.* studied draining foams comprised of initially monodisperse bubbles by both dielectric experiments and visual observations.[73] They reported that there is a link between drainage and coalescence, with the existence of a sharp destabilisation threshold controlled only by the liquid fraction of the foam. Results from this work showed that coalescence events do not directly depend on the size of the bubbles, instead coalescence was found to be dramatically enhanced below a critical liquid fraction, which is a function of both the nature of the surfactant and the concentration. This suggests that if the lifetime of a foam can be enhanced when the bubble size is reduced, because it

takes a longer time for drainage to occur in a fine foam and to reach the critical liquid fraction.

In situ X-ray tomography has also been employed as a way to image in real-time coalescence dynamics of both aqueous and metallic foams.[74,75] An example of this can be seen in Figure 7, which shows X-ray tomography images of a coarsening foams at varying times after production. [74] However, to move away from techniques that rely on counting and recognising individual coalescence events by eye, methods have been developed to automatically recognise such an occurrence.[76,77] Myagotin *et al.* have recently developed a projection imaging method completed with developed image analysis for studying coalescence processes in foams.[77] Their results showed real-time radiographic projection imaging of coalescence together with spatio-temporal image analysis. The analysis of different images of coalescence events images are based on the detection of breaks in the spatio-temporal images. This has proved to be a powerful technique for the quantitative analysis of coalescence processes accompanying the generation and temporal evolution of foams and emulsions.

3.4 Foam Destabilisation by Oil

Foams are commonly employed in enhanced oil recovery (EOR) as a way to both overcome complications associated with the process and to improve efficiency. The use of foams in EOR works by trapping bubbles in the porous media, reducing the gas relative permeability. Additionally, the presence of bubbles is act to increase the effective viscosity of the gas / foam phase.[78] Acting together, these mechanisms are thought to lead to a more favourable mobility ratio, which in turn improve displacement

efficiency of oil and contaminants in foam EOR.[78] Despite these favourable mechanisms, the main problem associated with the success of this technique is the adverse effect oil has on foam stability.[79,80] Even very small traces of oil or hydrophobic particles can strongly influence the stability of foam and it is known that three main mechanisms govern this destabilisation.[79] These mechanisms are: entry of oil droplet into gas-liquid interface, spreading of oil on the gas-liquid interface and formation of an unstable bridge across lamella.[18] The feasibility of these mechanisms occurring can be determined by evaluating the entering coefficient (E), spreading coefficient (S) and bridging coefficient (B), which are given in Equation 6, 7 and 8.

Equation 6:
$$E = \gamma_{wg} + \gamma_{ow} - \gamma_{og}$$

Equation 7:
$$S = \gamma_{wg} - \gamma_{ow} - \gamma_{og}$$

Equation 8:
$$B = \gamma_{wg}^2 + \gamma_{ow}^2 - \gamma_{og}^2$$

Where γ_{wg} is surface tension between surfactant solution and the gas, γ_{ow} is interfacial tension between oil and surfactant solution and γ_{og} is surface tension between the oil and gas.[80] These equations indicate that a positive entering coefficient ($E>0$) will lead to oil penetration into the air/ water interface and a positive spreading coefficient ($S>0$) leads to the spread of oil over the air/ water interface.[81] For foam rupture to occur, both of these conditions must be satisfied, such that the oil droplet must be able to invade the air/ water interface ($E>0$) and once the oil droplet has entered the air /water interface, it must be able to spread over the surface of the film ($S>0$). The spreading of the oil droplet over the surface of the film forces liquid out of the film into the Plateau borders and thus causes the film to become thin, ultimately leading to its rupture.[79] The final equation is concerned with the bridging coefficient (B), which is the effect that the bridging of oil

has on foam stability.[80] For example, if no spreading occurs ($S < 0$), the oil droplet will form a lens between the air/ water interface, which over a period of time will destroy the foam film if it is able to reach the lamella surface.[79] Therefore, positive B values will result in an unstable film, while negative values of B result in a stable film. This mechanism, first proposed by Aveyard *et al.*, was described for the antifoaming effects of hydrophobic particles and was later adapted to oil droplets.[48] Further information on this can be found in the defoaming section below (§5.4)

There are contrasting results found in the literature as to whether oil has an adverse effect on foam stability. For example, Andrianov *et al.* studied the effect different alkanes and crude oils had on the stability of nitrogen and air foams stabilised by a range of different surfactants.[82] Overall, their results found that the stability of foam was dependent on the carbon chain length of both the surfactant and the oil. As well as this, higher molecular weight alkanes and crude oils with high viscosities produced the least negative influence on foam stability compared to lower molecular weights. In term of surfactants, it was shown that a mixture of an anionic alpha olefin sulfonate along with a non-ionic fluorosurfactants gave the best foam stability in the presence of oils.

Osei-Bonsu *et al.* studied the stability of foams in presence and absence of oil on both the bubble and bulk scale.[79] By studying both the bulk and bubble scale in combination, a more comprehensive understanding of how the different physical properties of foams can control the stability could be identified. Four different surfactants were used: Triton X100, SDS, Cocobetaine and CocoSDS (a 1:1 ratio of Cocobetaine and SDS) (structures in Table 1). These surfactants were studied along with three different isoparaffin oils

were used (isopar G, isopar N, isopar V) which all varied in their hydrocarbon composition, viscosity, density and surface tension (isopar G lowest, isopar V highest). Results from both the bulk and bubble scale showed that CocoSDS gave the highest stability in the presence of oil, which was thought to be due to both the presence of the betaine within the mixture and due to the observed high viscosity. Additionally, the high viscosity of CocoSDS will lead to slower draining rates of the foam thus adding to stability. Again, foam stability in the presence of oil was found to be highly dependent on both the surfactant type and oil properties. Figure 8 shows how increasing the hydrocarbon composition, density, viscosity and surface tension of the oil (isopar G to isopar V) has a more favourable effect on the stability of the foam. On the bubble scale, from isopar G to isopar V there was a decrease in the rates of foam coarsening.

Previous work by Aveyard *et al.* and a review by Denkov are suggested for a more in-depth review of this area of foam stability.[48,83]

By understanding the ways in which foams become both stabilised and destabilised, it is possible to gain a lot more information on why foams are such an employed materials in both nature and industry. Next, the focus will be shifted onto why foams are such a desirable material for different applications and how their features are exploited for applications in both the man-made and natural world.

635 **4. In Nature**

636
637 Within a biological context, the stability of the foams must be resistant to microbial
638 degradation, predation, and other environmental challenges. Therefore, it is not
639 unexpected that biological foams and surfactant activity is relatively uncommon.
640 Proteins are ubiquitous in the natural environment and can act to stabilise foams, but
641 these are not the only natural surface active species. Stabilisation usually is a result of a
642 range of different materials, as outlined below.

643 644 *4.1 Sea foams*

645
646 Sea foams are produced by breaking waves that agitate water, allowing air to be
647 entrained. The resulting foams are usually quite weak and short-lived.[21] However, the
648 accumulation of impurities that stabilise the foam by acting as surfactants produces the
649 foam that can be blown inland as seen in Figure 9. Below the foam structure, layers of
650 bubbles occur that can be found in depths of up to 20 meters. The bubbles are thought to
651 be swept down by turbulent streams arising from breaking waves. These bubbles may
652 only be stable for about 10-60 seconds, whereas the stable foams that are blown far
653 inland may persist for up to 5 minutes.[20]

654
655 It is known that several surface-active compounds can cause sea foam, which mainly
656 consist of either proteins or dissolved organic carbon (DOC). According to Velimirov,
657 many seaweeds produce water-soluble mucilage, which are composed of polar
658 glycoprotein and exopolysaccharides can provide enough surface-active agents and
659 stability to induce foam formation.[84,85] A further important contributor to foam
660 formation has been found to be damaged phytoplankton cells, which release organic

matter. The enriched material is whisked into foam by the action of waves and washed ashore, where foam layers accumulate. Velimirov conducted an analysis of sea foam collected near kelp beds in South Africa.[84] His work revealed that the protein was the dominant component of the total drained foam suspension (22.85%), followed by total lipids (10.76%) and carbohydrates (3.07%). In another study conducted by Velimirov, the amount of individual sugar and lipid components in foam near kelp beds were investigated.[85] The results, taken from a 12 hour old drainage foam filtrate, showed a dominance of aldoses and deoxy sugars with β -mannose (32% of total carbohydrates) being the prevalent component followed by β -fucose (29%) and β -glucose (19%) (Table 1). The most important lipid class is represented by triglycerides, which amount to more than 50% of total lipids. Other natural occurring aquatic foams, for example foams found in rivers and streams, are usually linked to the presence of DOCs. DOCs usually occur in sediments, humic and fulvic acid substances, fine colloidal particles, lipids and proteins, saponins representing a family of plant glycosides and the decomposition products of phytoplankton containing carbohydrates and proteins.[86–90]

Most proteins are potentially susceptible to surface activity and inadvertent foaming will often lead to denaturation. As a result, denatured proteins often display surfactant properties, due to the exposure of hydrophobic groups (a more in depth discussion on protein stabilised foams can be found in section 2.2). Another factor promoting foam stability has been found to be the addition of salt. Lessard *et al.* investigated the effects of the addition of inorganic salts on the coalescence of bubbles.[91] Their results showed that there is a sharp transition concentration in which coalescence is dramatically reduced when salt is added. This concentration is characteristic of each salt investigated and in

some cases there was a 92.5% decrease in the coalescence from changing the concentration by 0.01M. Craig *et al.* found that bubble coalescence was inhibited by some salts, whereas others had no effect.[92] Another reason for salt increasing the stability of sea foams, according to Holmberg *et al.*, is because the salt concentration increases the surfactant critical packing parameter (CPP).[93] The CPP, as shown in Equation 9, where V is effective hydrocarbon chain volume, a_o is surface area of surfactant head group and l_c is length of the hydrocarbon chain, indicates how close surfactants are packed together at the air/ water interface and can therefore provide rough estimations of the shape of the micelle. Thus an increase in CPP will result in closely packed surfactants, an increased surface elasticity and viscosity and lead to high foaming ability and stability.

Equation 9:
$$P = V/a_o l_c$$

4.2 Foam nests

Numerous animals use foam nests as a way to protect their eggs or juveniles against environmental challenges, as well as providing a sufficient incubation environment during reproduction. Examples of this include several species of freshwater fish (e.g. armoured catfish *Hoplosternum littorale*) which produce floating layers of foam to protect their eggs (Figure 10 shows all of the animals discussed in this section).[9] The armoured catfish live in tropical environments where high temperatures and decaying organic matter create an oxygen depleted environment. For this reason, the foam nests provide an oxygen rich environment for developing eggs by supporting them in air on top of the water surface.[10] The catfish produces the foams by pumping water over the gills

710 whilst using its pelvic fins to mix the water with produced mucus, made from plant debris
711 carried by the male.

712
713 Foam nests are also observed in invertebrates, with the most commonly seen being the
714 cuckoo spit produced by the spittle bug. The foam produced has been found to be
715 predominantly for the protection of the larvae, being described as being able to adhere
716 mouthparts of potential enemies, like ants and spiders.[11] The liquid used for foaming
717 appears at the anus shortly after the insect begins to feed. Bubbles are blown into the
718 liquid from a canal formed by extensions of the abdomen, forming an enclosed space
719 under the abdomen into which air is drawn from outside the spittle. This air is then
720 blown into the liquid and the bubble produced are stabilised by a substance secreted by
721 the abdominal glands.[11] It is considered that the liquid secretion is of similar
722 composition to the juices of the host plant, but containing less sugar and amino-acids
723 because these have been utilised for nutrition.[94,95] There have been few studies on the
724 characterisation of the spittlebug foam so little is known on the composition and
725 molecular structure. One publication by Mello *et al.* reported that the foams are made up
726 of a complex and poorly characterised mixture of glycoproteins and proteoglycans, with
727 at least ten polypeptides being detected as well as traces of calcium.[96]

728
729 Among the largest of natural foam nests are those produced by different tropical and sub-
730 tropical tree frogs.[7,8] Depending on the species, the nests are adapted to persist
731 unharmed in many different locations including underground burrows, floating on
732 temporary pools, or high up in vegetation overhanging water as seen in Figure 11. An
733 example of a foam producing frog, which has been the subject of many studies, is the

734 mud puddle Túngara frog (*Engystomops pustulosus*) of Central/South America and parts
735 of the Caribbean. This frog species produces voluminous protein foam nests during their
736 mating season that are stable for several days under exposed tropical conditions, and
737 protect the developing embryos and juveniles against dehydration, predation and
738 microbial degradation.[12] Microbiological analysis showed that the foam nests can
739 remain stable for several days with no signs of organism growth.[13] Characteristic wet-
740 foam /dry-foam structures are observed under low magnification and depending extent of
741 drainage and age, the polyhedral dry-foam structure has been found to be predominant.
742 [13] Foam nests provide a more stable temperature environment and act as mini-
743 incubators to facilitate rapid development of eggs and tadpoles. Cooper *et al.*[12]
744 conducted a study in the wild and showed that temperatures within the foam nests are
745 usually slightly higher than the surroundings. This was found to be due to the occurrence
746 of a local greenhouse effect produced by solar radiation that is trapped within the
747 insulating foam. Additionally, the trapped air bubbles and restricted convection within
748 the foam reduces thermal losses, and this insulation serves to protect the developing eggs
749 against extremes of temperature fluctuation.

750
751 The creation of these foam nests usually occurs overnight during the mating season, they
752 are often found in large communal masses and remain attached to adjacent soil or
753 vegetation as water levels subside. To create foam nests, the female first produces eggs
754 and holds them together with a foam precursor fluid. The male then beats this mixture
755 into a white foamy mass, which incorporates the fertilised eggs, whilst clinging to the
756 back of the female and using his back legs in a rapid whipping motion.[97] The produced
757 foam has an overall density of around 0.1 g cm^{-3} , hence approximately 90% of the

758 structure is air, with the fluid phase made up mainly of water and secretions from the
759 frog. [12] Once this process is complete, the parents take no further interest in the
760 subsequent development of the frogs. The development of the eggs takes place 1–2 days
761 after the initial production of the nest and if there is sufficient water, the tadpoles are
762 ready to leave the nest at about 3 days under normal conditions.[13] However, in the
763 absence of developing eggs or tadpoles, these foam nests have been found to remain
764 stable and intact for at least 10 days in tropical conditions, amazingly, with signs of slight
765 dehydration but no sign of bacterial or fungal degradation.[13]

766
767 Surface tension and contact angle measurements of foam nests produced by túngara frog
768 have been carried out by Cooper *et al.*[12] The measurements were carried out with foam
769 fluids obtained by drainage, sonication or gentle centrifugation. Contact angle
770 measurements carried out using small droplets on a hydrophobic surface (Nescofilm)
771 showed excellent surface wetting, achieving comparable wetting as found in sodium
772 dodecylsulphate (SDS). The surface tension measurements, carried out with different
773 dilutions, showed a dramatic reduction from pure water to roughly 50 mN m^{-1} at total
774 protein concentrations of $\sim 1 \text{ mg ml}^{-1}$. The reduction in surface tension, and excellent
775 wetting characteristics of this material demonstrates how the attachment of foam nests
776 can readily attach to hydrophobic surfaces such as vegetation.

777
778 As previously mentioned, the production of stable foam nests does not include the use of
779 conventional small molecule surfactants, but rather requires the use of specialised
780 surfactant proteins in addition with a ‘cocktail’ of other molecules. These materials can
781 all act together to give longer term physical and biochemical stability in the natural

environment range as well as protecting the foams against microbial and parasitic attack. [7] The foam nest fluid has been found to contain 1–2 mg ml⁻¹ of total protein and a similar quantity of carbohydrate, which are predominantly comprised of complex cross-linked mixtures of O and N-glycans.[12] Additionally, there was found to be no detectable fat or lipid content (< 0.01 mg ml⁻¹), which reinforces the fact that there is an absence of conventional small molecule surfactant species. Electrophoresis analysis carried out in separate works [7,12] of the foam nest after removal of eggs shows a number of non-glycosylated proteins in the 10–40 kDa range. The more recent and detailed analysis of Túngara nest foam composition carried out by Flemming *et al.* found that the non-glycosylated 10-40 kDa range proteins are actually six major proteins within the foam, which have been labelled as ranaspumins (RSN-1 to RSN-6). [7] These proteins have not previously been identified and database comparison of these sequences emphasises a number of features relating to possible structure and function.[13] RSN-1 was shown to have some structural and sequence similarity with the cysteine proteinase inhibitor family, which suggests a possible antimicrobial role for this protein, however it does not appear to exhibit such activity. RSN-2 has an amphiphilic amino acid sequence unlike any previously reported and its relatively high abundance suggests that it might be one of the major surface active components. The further four proteins (RSN-3 to RSN-6) are lectins, three of which (RSN-3 to RSN-5) are similar to each other and show sequence similarities to fucose-binding proteins found in certain species of fish but not previously identified in a land vertebrate. Further work by Cooper *et al.*[12] has utilised neutron reflection to quantitatively determine both the surface excess and layer thickness of these ranaspumins. Over the concentration range 0.001 – 0.5 mg ml⁻¹, the results obtained

showed how the surface excess increased persistently with increasing concentration from 0.56 – 4.4 mg m⁻². Fitting the measured NRW reflectivity profiles at the lowest concentrations, suggested the presence of a monolayer with a thickness of ~13 Å. At the highest concentration, the layer thickness was found to increase to ~75 Å. This large increase was determined to contain three different regions: top layer ~20 Å, middle layer ~30 Å and a submerged layer ~25 Å into the bulk solution.

Although foams are rarely found in the natural environment, when they are it is fascinating to explore how they are exploited for a desired effect. Many of the same structural and physical properties of foams are of great interest in different industrial processes, as are described below.

5. Synthetic and Industrial Foams

Foams have many desirable properties for applications due to their very large surface area, their lightness and the fact that they exhibit both solid and liquid behaviour. These features, lend themselves to the functional and/ or structural foam-based materials that appear in many different industrial processes and products. To give some perspective, the global polyurethane foam market alone is expected to reach ~ \$72 bn per year by 2020.[98]

There are four main types of foams used industrially: aqueous, solid polymer, edible polymer and ceramic foams. Edible polymer foams are easily recognisable, examples include bread, sponge-cake or chocolate mousse, and are stabilised by surface active agents such as proteins, fats and alcohols within the food production.[99] Aqueous foams are the most widely used and have many different applications from the cosmetics

industry to fire-fighting. Fire-fighting foams are so effective due to their ability to extinguish liquid fuel fire by isolating, confining and smothering. Additional examples include the use of foam sprays loaded with irritating materials which are used in law enforcement or self-defence [21] and a more recent use has been found in sport, labelled as vanishing foam, which allows referees to provide a temporary visual distance marker for the players.

Soft solid polymer foams are often used as packaging materials or cushioning for furniture. Hard polymer foams are generally used as lightweight structural elements in the construction industry, for example as thermal insulators or noise reducers. Solid polymer foams are also used as energy absorbers as a way to muffle explosions in mine clearances. The ability to quickly fill large spaces, is advantageous for rock excavation, where foam is injected into rock or concrete in a controlled way to fracture and excavated them.[100]

Ceramic foams are rigid and lightweight materials, which are produced by first producing a slurry of finely ground ceramic particles, a foaming agent and a setting polymer. The slurry is then whipped to entrap gas and is poured into a mould, which sets at room temperature to form a solid body. After which, the slurry is fired to sinter the ceramic particles together to form a strong porous ceramic body.[101] The foams are mainly silicon based (SiC , Si_3N_4) and for this reason, they can be used in high temperature environments, for example high temperature metal filtration, catalytic combustion devices and more recently catalysis.[102,103]

Foam formation is not always desirable and a number of industries are directly affected by the problem of unwanted foam. This can be problematic, as foams can obstruct gas transport and render the process of interest ineffective, with significant cost implications. For this reason, antifoaming and defoaming agents exist as a way to inhibit the production of unwanted foam by-product.[20,21] The next sub-sections will cover a select range of industrial foams, as well as the use of antifoaming and defoaming materials.

5.1 Fire-fighting foams

Water has long been the universal agent for suppressing fires, but it is ineffective for oil or liquid fuel fires. For this reason, fire-fighting foams were invented initially as a way to effectively extinguish oil fires. The first mention of using foam to fight fires was by British scientist J. Johnson, who first patented the idea for fire-fighting foam in 1877. His idea was that, due the frothy condition and low density of the foam, it will be able to starve a fire of any oxygen by floating on the surface of “fatty bodies” such as petroleum.[104] He recommended that the chemical foam was to be made by mixing two liquid solutions, one containing sodium bicarbonate and saponine and the other containing aluminium sulphate. It was not until 1904 that the first test of this work was conducted. Aleksandr Loran, a Russian engineer, was able to successfully use the chemical foam during an 11-metre diameter naphtha storage tank fire in Russia.[105] During the period of 1920-1930, there were many advances in the field of fire-fighting foams. Firstly, the discovery that a proteinaceous product, which could be easily dissolved in water, can be extracted by chemical hydrolysis from organic by-products such as hoof and horn meal. From this, it was established that protein foam concentrates

were far superior to previously mentioned synthetic foam stabilisers. However, early experiments proved that the water base of protein foams rendered them ineffective on alcohol fires, due to the miscibility of water and alcohol. This led to the development of early chemical foams with alcohol resistant properties. The next major advancement during this period was in the way the foams were produced and delivered, leading to the development of ‘mechanical foams’ which can expand up to 10 times the volume of the solution. This was achieved by introducing the protein foam concentrate into a flowing water stream, whilst air was added to produce finished foam. Further extensive experimental work on the topic of mechanical foams led to the development of the first high-pressure air injection systems.[105] This system works in the same way as the previously mentioned method, but uses very high pressures, and thus foam can be propelled at a much larger distance.

There was a significant expansion in the market for both foam concentrates and delivery equipment during World War 2. Fire-fighting foams were in high demand from both industry and the armed forces. The standard foam concentrate during this time was 6% and used plant extracts as stabilisers, primarily saponine or liquorice. However owing to the high cost of these raw products, they were replaced by other extracts and by-products of the paper industry, or protein hydrolyses. This substitution of additives allowed the foam concentrate volume to be reduced from 6% of the solution to 3%, which lead to an urgent demand for the new stronger concentrate. The advantages of this new 3% concentrate were that storage space, weight and transportation costs could all be reduced.[104]

From 1950-1990 saw developments mainly in the formation of new types of fire-fighting foams, with many of the new development using synthetic surfactants to produce the foam concentrates. Additionally, these synthetic concentrates were able to produce low, medium and high expansion foams. The introduction of fluorochemical surfactants into both protein and synthetic foam compounds occurred in the 1960's, which helped to improve both the flow and fuel tolerance properties of existing foams. The addition of fluorocarbon surfactants into protein foams produced what is known now as a fluoroprotein (FP) type foams, and in the case of synthetic foam, Aqueous Film Forming Foams (AFFF) were produced.[104] During the 1970's initial developments of alcohol resistant foams were undertaken continuing until the 1980's. These were multi-purpose foams for use with both hydrocarbons and polar solvent fires. Polymeric-type alcohol resistant foams were established during the 1980's, which gave better separation between the foam layer and the liquid level and avoided the problem of alcohol/water mixing. Additional advances using these polymeric-type foams during this time were the production of foam concentrates, known now as alcohol resistant aqueous film forming foams (AR-AFFF), film-forming fluoroprotein (FFFP) and alcohol resistant film-forming fluoroprotein (AR-FFFP). More information on different fire-fighting foam types and their different uses will be given below.[104,105]

From the 2000's up until now, the main aims in fire-fighting foams have been to try and move away from the use of PFOS (perfluorooctanesulphonate) and PFOA (perfluorooctanoic acid) (Table 1) in AFFF foam concentrates, as well as developing new fluorine-free fire-fighting foams (FF). All AFFF type foams are known to contain fluorosurfactants; with the most common being the two just mentioned PFOS and PFOA.

The reason why the fire-fighting industry has moved away from the use of these chemicals is a result of legislative pressures, as it is now well recognised that many fluorochemicals have a potential impact upon the environment and human health due to pronounced persistence of their degradation products, variable degrees of bioaccumulation potential and toxicity. Advances in fluorine-free fire-fighting foams have seen them meeting international approvals for fire-fighting requirements, whilst at the same time being environmentally more benign.[106–108] Recently, Vinradov *et al.*[109] reported the development of new fire-extinguishing agents which involve the use of self-hardening silica-based sol-gel foams. The silica-based sol-gel foams were produced by injecting an aqueous solution of acetic acid (20-50% volume) into a mixture of 6% volume aqueous based surfactants (SDS) with 10-50% volume sodium silicate in a commercially available fire extinguisher (Figure 12). The resulting foam consisted of organised silica nanoparticles with narrow particle size distributions (~10-20 nm). Results from live fire tests showed that the silica-based sol-gel foam could extinguish a wood fire in ~5 seconds, compared to water and an AFFF foam which extinguished the fire in ~35 seconds and ~20 seconds respectively. In addition to this, due to the excellent thermal stability of the silica foam, no signs of reignition after exposure to a direct flame was detected, whereas reignition was observed for both water and the AFFF.

As previously mentioned, fire-fighting foams were developed primarily to deal with the hazards posed by liquid fuel and oil fires. The reason for this is the ability of the foams to extinguish burning hydrocarbons more effectively than water due to their low density and because they float on the fuel. Fires have three needs in order to spread and persist, which are oxygen, fuel and heat. Once one or all of these three supplies are exhausted,

the fire will stop. Fire-fighting foams can attack all three at the same time by excluding oxygen from the fuel surface, cooling the fuel to below the ignition point by forming a radiant heat barrier which can help to reduce heat feedback from flames to the fuel, and lastly by trapping the fuel vapour at the liquid surface.[20] Additionally, for a fire-fighting foam to be recognised as effective, it should remain undamaged as long as possible so that the risk of re-ignition is reduced. This suggests that a slow draining foam with a high liquid fraction desired so that a strong heat resistance can be achieved.

Fire-fighting foams are classified according to their liquid fraction (Equation 1) or expansion ratio (ϕ_l^{-1}) into low (5:1 to 20:1), medium (up to 200:1) and high expansion foams (up to 1000:1). Expansion ratio is defined as the ratio of the volume of the finished foam to the volume of the foam solution used to produce it. Low and medium expansion foams are created by use of a branch pipe, which is the device that aerates the foam concentrate to produce the finished foam. These foams can be sprayed from a distance of up to 10-20 metres.[20] High expansion foams are produced in a different way to low and medium expansion foams. The foam concentrate is sprayed onto a net or gauze through which air is being drawn or blown to produce the high expansion. As a result of high expansions, these foams are too lightweight to be projected over any practical distance, and must be applied directly to the fire. As the expansion ratio is increased, the ratio of water in the finished foam decreases, this has an adverse effect on the heat resistance of the foam. Also, the low density of the foam causes problems for outside applications, where the foam might be blown away by wind.[20]

975 Practically foam formulations are supplied as liquid concentrates, they are generally
976 supplied by manufacturers as 6% (6 parts foam concentrate in 94 parts water), 3% or 1%.
977 All different fire-fighting foam types contain water, solvents and stabilisers, however, the
978 different components contained in the different types of foams and the advantages of
979 each foam are shown in Table 2.

980

981

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Fire-fighting Foam Type	Main Components	Uses	Advantages of Foam
Fluoroprotein	Fluorinated surfactants and formulated hydrolysed proteins	Mainly used on hydrocarbon fires	<ul style="list-style-type: none"> - Flow quicker than standard protein foams - Forms very stable foam blankets which re-seal if ruptured and have very good burn back resistance - Very good vapour suppression
Film-Forming Fluoroprotein	Based on the same components as Fluoroprotein, but with the addition of film-forming fluorinated surfactants	Mainly used on hydrocarbon fires	<ul style="list-style-type: none"> - Flow quicker than fluoroprotein foams - Produces fast flame extinguishment due to formation of films - Forms very stable foam blankets which re-seal if ruptured and have very good burn back resistance - Produces very stable foam blankets on both hydrocarbon and polar solvent fires for superior extinguishment, vapour sealing and burn back resistance - Re-seal if ruptured
Alcohol-Resistant Film-forming Fluoroprotein	Based on the same components as Film-Forming Fluoroprotein, but with the addition of a polysaccharide polymer	Used on hydrocarbon fires and can be used on polar solvent fires	<ul style="list-style-type: none"> - Produces very stable foam blankets on both hydrocarbon fires for extinguishment and burn back resistance - Re-seal if ruptured
Aqueous Film-forming Foam	Fluorinated film-forming surfactants	Mainly used on hydrocarbon fires	<ul style="list-style-type: none"> - Produces very stable foam blankets on both hydrocarbon fires for extinguishment and burn back resistance - Re-seal if ruptured
Alcohol-Resistant Aqueous Film-forming Foam	Based on the same components as Film-Forming Foam, but with the addition of a polysaccharide polymer	Used on hydrocarbon fires and can be used on polar solvent fires	<ul style="list-style-type: none"> - Produces very stable foam blankets on both hydrocarbon and polar solvent fires for superior extinguishment, vapour sealing and burn back resistance - Re-seal if ruptured

984					- Low environmental i
985	Table 2:	Fluorine Free Foams	Hydrocarbon surfactants and polysaccharides	Mainly used on hydrocarbon fires and jet fuel	and are 100% biodegra
986	Showing				- Exceptionally stable i
987	the				term storage
988	different		A mixture of high activity hydrocarbon foaming agents and stabilisers	Used on hydrocarbon fires typically in large, open areas like aircraft hangers etc.	- Able to fill large area
989	types of	High Expansion Foams			quickly, therefore comj
990	Fire-				engulfing the fire

Fighting foams and their uses. Information adopted from following sources.[105,110]

5.2 Mineral Flotation

The mineral floatation process is the most important method of concentrating minerals. It was first developed over one hundred years ago, and since then has contributed largely to the expansion of the raw materials industry.[111,112] The principle of mineral flotation is to separate minerals from ore by taking advantage of differences in the wetting properties of each. Differences in hydrophobicity between valuable minerals and waste gangue (low value waste material) are increased through the use of surfactants and wetting agents. When the process was first implemented, naturally occurring chemicals such as fatty acids and oils were used in large quantities to increase the hydrophobicity of the mineral. However, since then, the process has been adapted and now uses close to 90% of the world's surfactant products.[21] For a more in depth overview of the history of mineral flotation, the reader is referred to the following sources.[111,113,114]

The process, shown schematically in Figure 13, begins with an ore-containing rock being extracted from the ground. It is then ground up and treated in order to separate minerals, such as sulphide, copper, zinc or nickel from gangue. This initial separation step needs to

1012 be very fast and inexpensive, and typical speeds are of the order of one hundred tonnes of
1013 mineral per hour. The ground up rock and minerals are then placed in tanks with the
1014 addition of at least two surfactants, which have different effects. One surfactant is used
1015 to control the affinity of the mineral to the interface and one causes the mixture to foam.
1016 It is possible to optimise the physico-chemical conditions (pH, nature and concentration
1017 of surfactant) so that the mineral grains are trapped by the interfaces while the gangue
1018 remains in the liquid. The ores that are low in metal content have hydrophilic character,
1019 and so are wetted and drain through the foam, on the other hand, components rich in
1020 metal are hydrophobic and remain in the foam.[20] Foams are useful for this application
1021 due to their ability to trap substances as well as having very high interfacial areas. The
1022 mixture is then vigorously mixed whilst air is injected at the base; this is done in such a
1023 way to favour encounters between bubbles and particles. During these encounters, the
1024 gangue particles can be trapped in the liquid phase and therefore sink to the bottom of the
1025 tank. Conversely, foam is continually formed and rises to the surface of the tank before
1026 spilling out over the top, bringing with it the mineral attached to the bubbles. During the
1027 ascent, a large proportion of the liquid drains back down through the foam, making it dry
1028 and fragile which is beneficial for the recovery of just the mineral. Additionally, the low
1029 density of the foam allows it to float on the surface where it can be skimmed off. [21]
1030
1031 The attachment of hydrophobic particles to gas bubbles is one of the most important steps
1032 in the mineral flotation process. After the particles collide with rising gas bubbles, they
1033 attach to each other to form stable particle–bubble aggregates. Three independent sub
1034 steps can describe this particle–bubble interaction: collision, attachment, and stability.

The effectiveness of the whole process of particle–bubble capture is usually represented by the product of the efficiency of each sub step as seen in quation 10.[115]

Equation 10:
$$E_{cap} = E_c E_a E_s$$

Where E_{cap} , E_c , E_a , and E_s are the capture, collision, attachment, and stability efficiencies. The capture, collision, and attachment efficiencies are defined as the fraction of particles captured by a bubble, the fraction of particles colliding with a bubble, and the fraction of colliding particles, which actually attach to the bubble surface.[115]

5.3 Recent advances with foams

Metallic foams are one of the most recent advances, where the term foam in its original sense is reserved for a dispersion of gas bubbles within a solid, liquid or gel. Metallic foams are also referred to as solid foams, materials having cellular structures made up of a solid metal containing a large volume fraction of gas-filled pores. [116] The pores can be either sealed to produce closed-cell foams, or an interconnected network, which form open cell foams. The closed-cell foam is referred to as metal foams, whereas the open-cell foam is referred to as porous metal.

There are a few different ways in which metals can be foamed.[116,117] The methods employed most regularly are either to create gas bubbles in a metallic liquid melt or by powder metallurgy. The process of powder metallurgy begins with the mixing of metal powders, which are elementary metals, alloys or powder blends with a foaming agent. A common example of a foaming agent for aluminium alloy foam production is TiH_2 ; this

is because the temperature at which it begins to decompose is close to the melting temperature of the alloy.[118] Additionally, space holders are added to give space to the open pores during or after the foam making process. After all of these materials have been mixed, they are then compacted by processes to ensure the foaming agent is embedded into the metal matrix without any residual open porosity, yielding a dense, semi-finished product. The final step is to heat the mixture to temperatures near the melting point of the metal alloy. The foaming agent, which has been distributed evenly within the alloy, decomposes and in the process, releases gas forcing the compacted material to expand into its highly porous structure.[117] The other method mentioned to produce metal foams, achieves it by creating gas bubbles within metallic melts. Due to the high buoyancy forces in the high-density liquid, the gas bubbles tend to rise to the surface of the melt. However, the viscosity of the metallic melt is increased to inhibit this from occurring, achieved by adding fine ceramic powders or alloying. Three ways of foaming metallic melts are:

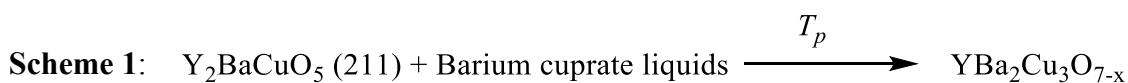
- Injecting gas into the liquid metal from an external source
- Causing the nucleation of gas bubbles that have just been dissolved in the liquid
- Causing an in-situ gas formation in the liquid by admixing gas-releasing foaming agents to the melt

Metallic foams have properties such as such as low density, good energy absorbing capabilities, high stiffness and low thermal conductivity, making them very sought after materials in a number of different industries such as building, aerospace, biomedicine and many more.[116] The most prominent property of a metal foam is its low density, for

1085 example aluminium foams usually range from 0.4-1.0 g cm⁻³, although values down to 0.2
1086 g cm⁻³ have been achieved.[117]

1087
1088 More recently, a new superconducting foam material has been reported.[119] Much like
1089 bulk and thin film superconductors, which have their own strengths and weaknesses,
1090 foams form superconductors that are attractive for certain applications. These materials
1091 have been said to provide solutions for some problems encountered in applications of
1092 bulk or film-type semiconductors, such as reducing hot-spot formation or by decreasing
1093 thermal inertia. YBa₂Cu₃O_y (Y123) foams, shown in Figure 14, have the macroscopic
1094 shape of bulk materials but revealing struts with a thickness of only a few tenths of a μm
1095 that could effectively be used as resistive elements in superconducting fault current
1096 limiters. The small thickness of the struts allows a more efficient heat extraction from the
1097 superconductor during or after faults as compared to the same material in the bulk form.
1098 Examples of other benefits of using the foam structure include a high thermal shock
1099 resistance and a more uniform and more rapid oxygenation heat treatment.[120]

1100
1101 The production of Y123 foam superconductor begins with the fabrication of a porous
1102 Y211 foam by a common ceramic foam manufacturing processes (Scheme 1, below).
1103 This process continues with the impregnation of a reticulated polyurethane foam of
1104 desired porosity with a Y211 slurry, and then heat treatment to burn off the polymer. The
1105 second stage involves the penetration of the produced Y211 foam by molten barium
1106 cuprates and copper oxides followed by a controlled growth of the Y123 phase at the
1107 peritectic temperature (T_p). The produced Y123 superconductor foam grows as a single
1108 grain in the presence of a seed crystal.[119]



These novel materials have been said to be an important step forward to obtain large, but lightweight superconducting bulks, which will be important for several applications like the all-electric plane or applications in space.[121]

5.4 Defoaming

The subject of defoaming is large, multi-faceted and involved, and detail is beyond the scope of this review, however, a brief account will be given below and more in depth accounts can be found elsewhere.[14,16–18] The control of foaming dates back to the start of the 20th century, when there were two main methods employed to prevent foaming - mechanical devices and chemical additives.[122] A few examples of the mechanical methods utilised to reduce volumes of excess foam were pulsing jets of air above the liquid, ultrasound, centrifuges or changing pressures.[16,122,123] However, there were problems associated with the mechanical methods were mainly down to expense due to the high energy demands. More preferable chemical methods were then designed. Early chemical additives, which were only present in small quantities, included alcohols such as caprylic alcohol, amyl alcohol, octyl alcohol, trimethylcyclohexanol, oils such as, linseed oil, castor oil, rapeseed oil, kerosene, and many others.[122,123] Oils are still used to this day as defoaming agents, however, new developments saw the introduction of hydrophobic solid particles and surfactants (or a mixture) into the field of defoaming.

1136 The industries that commonly employ defoaming agents include pulp and paper
1137 production, food processing, textile dyeing, fermentation (in both drug and food
1138 manufacturing) and industrial waste treatment.[14,83] Additionally, defoaming is also a
1139 very important factor in the previously mentioned mineral flotation process. However, in
1140 the oil industry there are significant challenges in both crude oil production and oil
1141 refining. The use of defoaming agents on entry into a gas-oil separator is well
1142 studied[14] and the primary types of agent employed are polydimethylsiloxanes and, for
1143 particularly difficult or aggressive crude oils, fluorosilicones.[14] The process for the
1144 addition of these materials occurs upstream from the separator to ensure a homogeneous
1145 dispersion throughout the crude oil.[14]

1146
1147 Whenever foams are produced during these processes, it leads to a reduction in product
1148 and process efficiency, which ultimately leads to loss of revenue if untreated.[14] The
1149 most noticeable and easy to monitor problems associated with excessive foaming occur
1150 with foams which form and float on surfaces. Surface foam can cause problems with
1151 liquid levels and results in overflow; other problems relating to the formation of foam
1152 include reduction of reduced capacity storage tanks, bacterial growth, dirt flotation/
1153 deposit formation, reduced effectiveness of the fluids, eventual downtime to clean tanks
1154 and drainage problems in sieves and filters, etc.

1155
1156 Oil and particles have been added into the foam systems for many years with the
1157 development of antifoams.[15] Example of typically used solid particles is inorganic
1158 silica, Al_2O_3 , TiO_2 , or polymeric materials such as polyamide and polypropylene.[14] If
1159 particles are hydrophilic, foam stability is enhanced since particles collect in the Plateau

borders, which slows down film drainage. However, if particles are hydrophobic, they can enter the air/ water surfaces of the foam and cause destabilisation via the bridging-dewetting or bridging-stretching mechanism. This is thought to be the mode of action of the defoaming process by particles: Figure 15 shows how hydrophilic and hydrophobic particles affects the stabilisation and destabilisation of foams.

3. Conclusions

Stabilisation and destabilisation are the most common studied features of foams and there are many papers published every year. This review has aimed to provide an up-to-date account of how aqueous foams are stabilised and destabilised, with focus being on relevance both naturally and industrially. Foams have many features and properties which make them a useful in both the man-made and natural world. The ability to exploit foams for their very large surface area, lightness and ability to act as both a solid and liquid is what lends them to many different areas of science and engineering.

Additionally, the use of superconducting foams[119–121] and metallic foams[116–118] have also been explored, which have prospective uses in industries such as aerospace, shock absorbing, light-weight building and many more, thus showing the potential for further development in the near future.

Novel ways of visualising the destabilisation of foams, ranging from magnetic resonance imaging to neutron reflectivity, have been identified.[54,63–66,71,74,75,77] The combination of the background physics and mathematics, along with the always-improving ability to image in real time these destabilisation mechanisms provides a great scope for an in-depth understanding of foam stabilisation and destabilisation, which will

be advantageous to many different industries and scientific communities. As a result, the area of foams remains a very important and exciting field of research.

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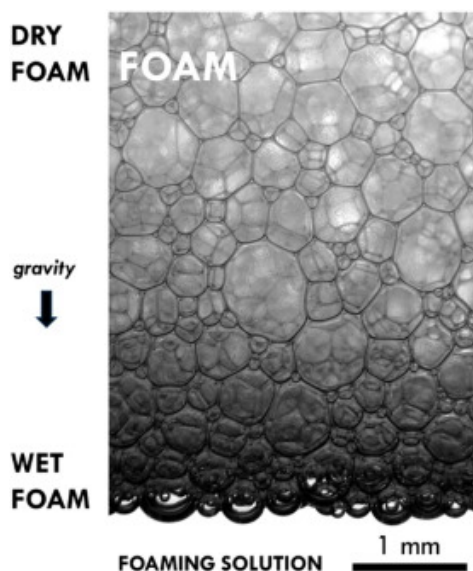


Figure 1: Showing liquid drainage. Reprinted with permission from ref 2. Copyright 2015 Elsevier.

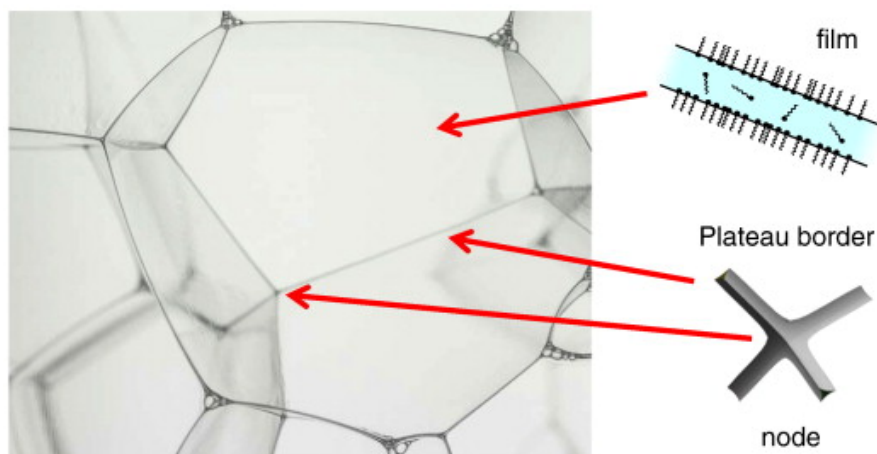


Figure 2: Showing how surfactants pack on a foam film surface. Reprinted with permission from ref 1. Copyright 2014 Elsevier.

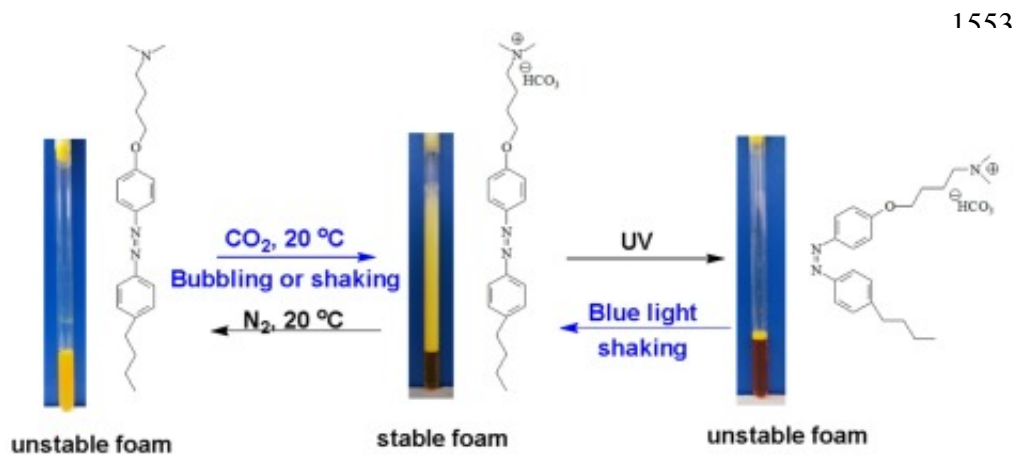


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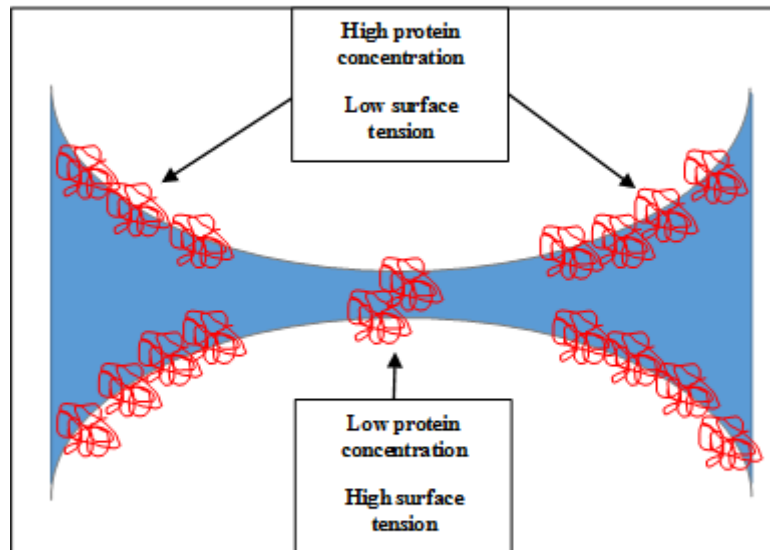


Figure 4: Gibbs Marangoni effect present in protein stabilised foams.

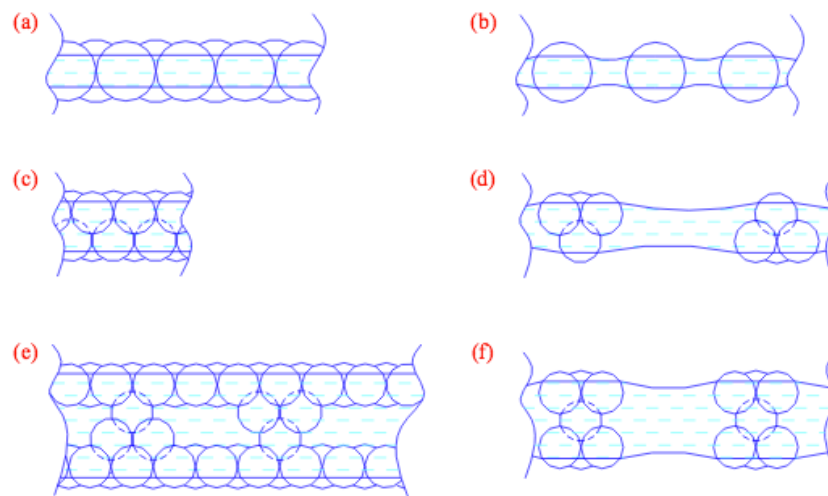


Figure 5: Showing the six different particle arrangements that can effectively separate the two air/ water interfaces. (a) CP1, (b) LP1, (c) CP2, (d) LP2C, (e) CP2+, (f) LP2+C. Reprinted with permission from ref 45. Copyright 2003 Elsevier.

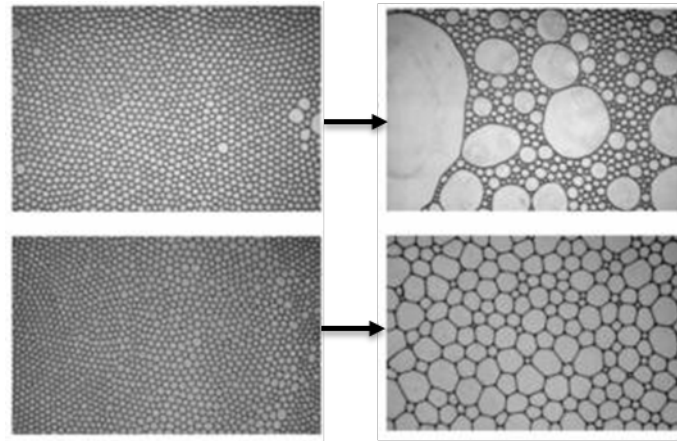


Figure 6: Top image shows coalescence and lower image shows coarsening

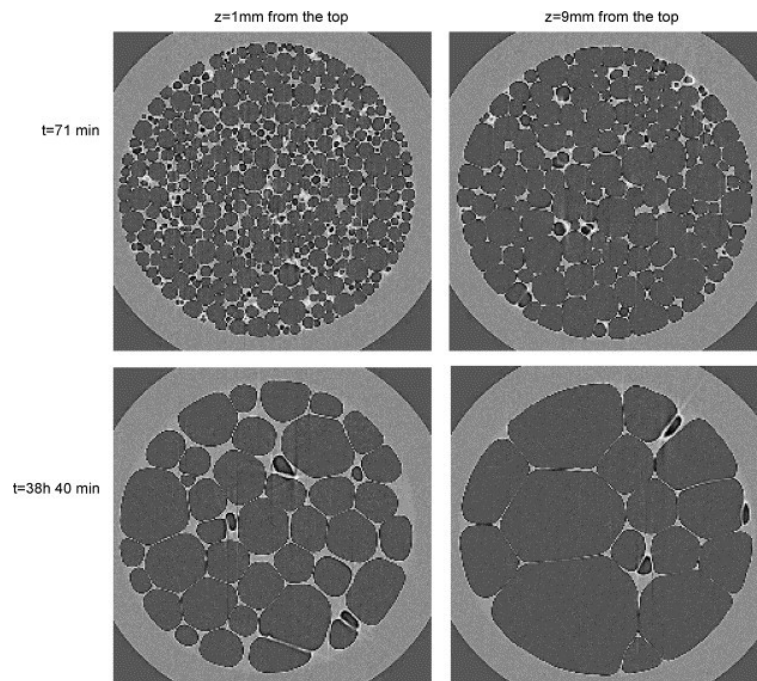


Figure 7: Four slices recorded at 1mm (left) and 9mm (right) from the top of the scanned volume, 71 min (top image) and 38h 40 min (bottom image) after the

making of the foam. Reprinted with permission from ref 74. Copyright 2005 Elsevier.

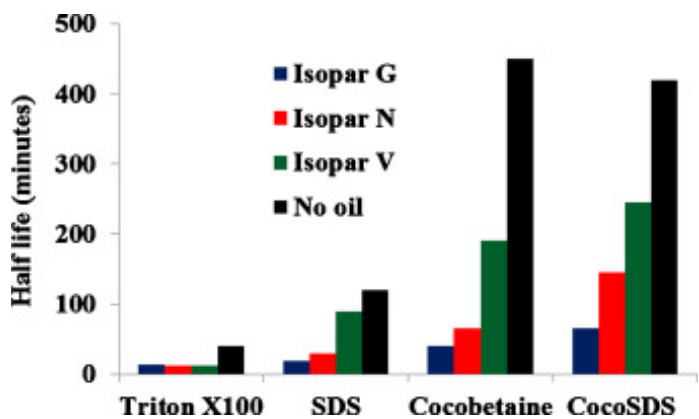
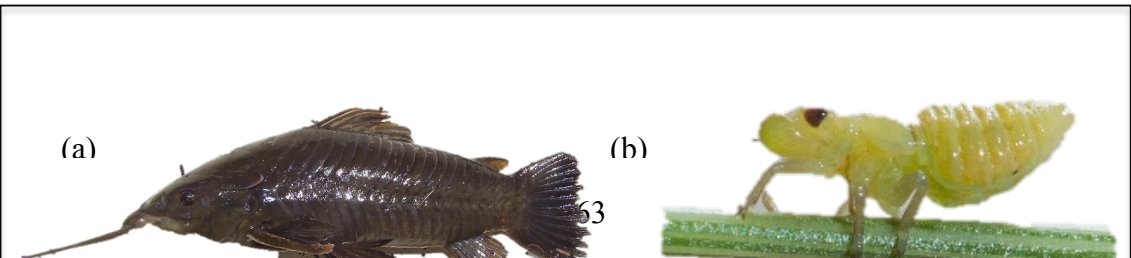


Figure 8: Showing foam stability in presence and absence of different hydrocarbon oils. Reprinted with permission from ref 79. This article is available under the terms of the creative commons attribution license (<http://creativecommons.org/licenses/by/4.0/>)



Figure 9: Showing a typical sea foam (image taken by author).



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Figure 10: Showing the different animals discussed in this section. (a) Armoured catfish (*hoplosternum littorale*), this article is available under the terms of the creative commons attribution license (<https://creativecommons.org/licenses/by-sa/2.0/deed.en>). (b) Spittle bug, photo reprinted with permission from David Iliff. License: CC-BY-SA 3. (c) Túngara frog (*Engystomops pustulosus*), photo is free to use from the public domain (<https://creativecommons.org/publicdomain/mark/1.0/>),



Figure 11: Showing foam nest produced by African tree frog (left) and the armoured catfish (right). Reprinted with permission from ref 12. This article is available under the terms of the creative commons attribution license (<http://creativecommons.org/licenses/by/4.0/>)

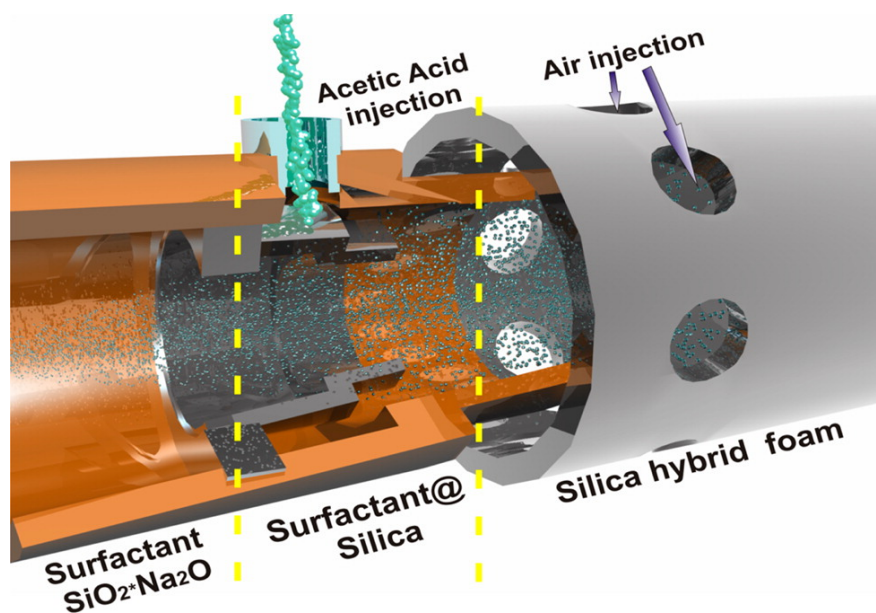


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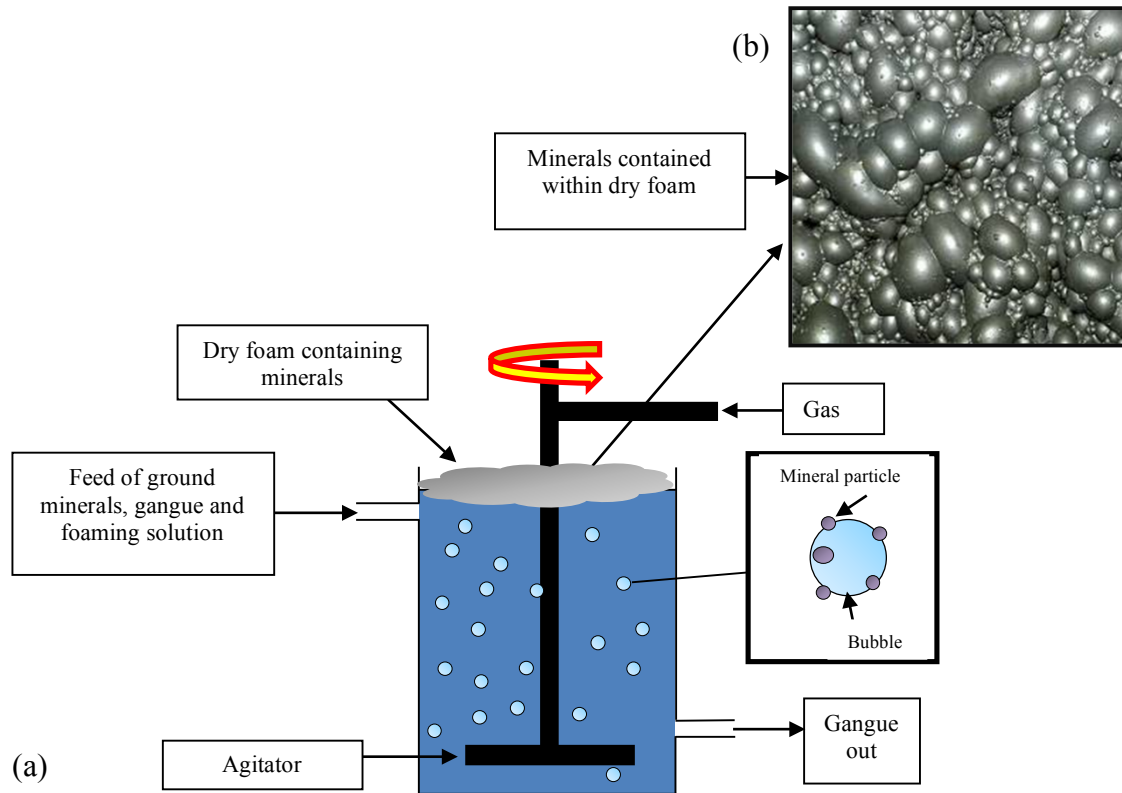


Figure 13: (a) Schematic of Mineral Flotation Process. (b) Close up image of mineral containing foam from a mineral flotation process. Reprinted with permission from ref [124]. This article is available under the terms of the creative commons attribution license (<http://creativecommons.org/licenses/by/4.0/>)

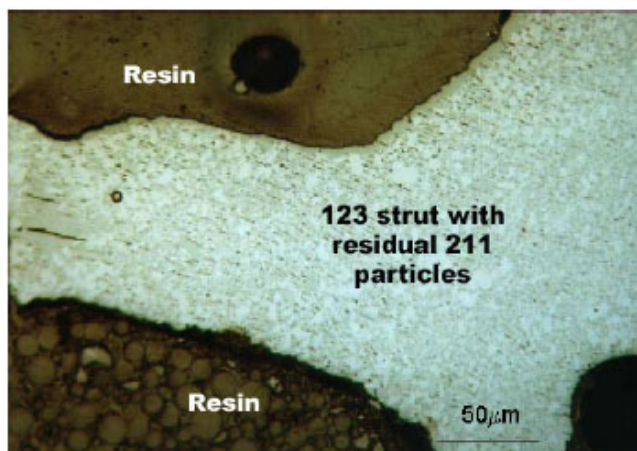


Figure 14: Microscopy image of Y123 superconducting foams. © IOP

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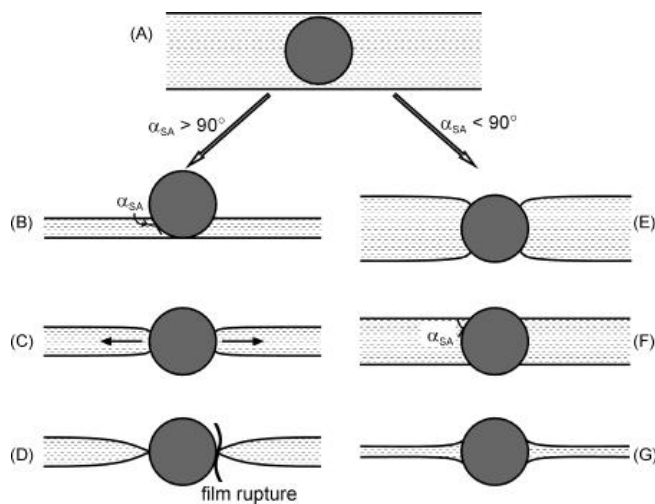


Figure 15: (B-D) shows the process of defoaming in the presence of sufficiently hydrophobic particles ($\alpha_{SA} > 90^\circ$). (E-G) shows how if particles are sufficiently hydrophilic ($\alpha_{SA} < 90^\circ$), the particle is not dewetted and the foam film remains stable.

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